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Citation: Shirtcliffe, Neil, McHale, Glen, Newton, Michael, Perry, Carole and Pyatt, F. Brian (2006) Plastron properties of a superhydrophobic surface. Applied Physics Letters, 89 (10). pp. 104106-104108. ISSN 0003-6951

Published by: American Institute of Physics

URL: <http://dx.doi.org/10.1063/1.2347266> <<http://dx.doi.org/10.1063/1.2347266>>

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N.J. Shirtcliffe, G. McHale, M.I. Newton, C.C. Perry and F. B. Pyatt, *Plastron properties of a superhydrophobic surface*, Appl. Phys. Lett. **89** art 104106 (2006); DOI:10.1063/1.2347266.

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Plastron Properties of a Superhydrophobic Surface

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Abstract

Most insects and spiders drown when submerged during flooding or tidal inundation, but some are able to survive and others can remain submerged indefinitely without harm. Many achieve this by natural adaptations to their surface morphology to trap films of air, creating plastrons which fix the water-vapor interface and provide an incompressible oxygen-carbon dioxide exchange surface. Here we demonstrate how the surface of an extremely water-repellent foam mimics this mechanism of underwater respiration and allows direct extraction of oxygen from aerated water. The biomimetic principle demonstrated can be applied to a wide variety of man-made superhydrophobic materials.

PACS Numbers 68.08.Bc (Wetting), 68.03.Cd (Surface tension), 89.20.-a (Interdisciplinary applications of physics), 87.68.+z/87.23.-n (Biomaterials and biological interfaces/ Ecology and evolution)

Keywords Super-hydrophobic surfaces, plastrons, wetting

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Super-hydrophobic water-repellent surfaces are common in nature and, amongst plants, have the function of keeping the surface dry and free from dust and pathogens due to their self-cleaning properties under the action of rain.^{1,2} These types of surfaces enhance chemical hydrophobicity from wax layers by micro- or nano-scale surface structuring to achieve contact angles to water of 150° or higher. Man-made materials using this combination of chemical functionality and small-scale topography to create water-repellent surfaces are important for industrial applications such as stain resistant textiles, reduction of frictional drag in water and self-cleaning windows.³ A principal feature of these surfaces is the suspension of a droplet of water on surface protrusions so that the water effectively sits upon a composite solid-air surface with a solid fraction of 20% or less.⁴⁻⁶ The droplet of water is then effectively separated from the solid by a layer of air. We observed that when such a superhydrophobic surface is immersed in water it glistens with a silvery sheen, thus indicating that a sheathing film of air remains on the submerged surface. Such silvery reflections are also observed from the plastrons on some aquatic insects and spiders.⁷⁻¹⁰ Plastrons are an adaptation to the water environment that allows oxygen to be extracted directly from the surrounding water. We therefore considered whether the submerged surface of a superhydrophobic material could be used to mimic plastron respiration rather than be simply a passive water-repellent surface. Given that these materials gain their superhydrophobicity by dramatically reducing the solid fraction of their surface area, it might be naively expected that submersion would necessarily cause water penetration and a loss of superhydrophobic properties thus preventing their use for plastron respiration.

Even when fully saturated the oxygen concentration in water is around thirty times less than in air. Some diving insects resolve this problem by carrying an air bubble that provides both an air reservoir and a water-vapor interface across which gaseous diffusion occurs, thus allowing oxygen to be replenished and carbon dioxide to escape.¹¹ Such an air bubble will eventually collapse due to nitrogen slowly dissolving

into the water. Other aquatic insects, such as the great diving beetle *Dytiscus marginalis*, have morphological adaptations on their abdomen consisting of rigid non-wettable hairs, which support a non-collapsible film of air (a plastron). This ensures the film of air is permanent and of constant volume.⁹ It has also been reported that the silk nests of some terrestrial, ground dwelling spiders act as a physical gill extending survival times following flooding by factors of 7 to 16.¹² Plastron structures formed by a hydrophobic open mesh network are also found in the cocoons of some silk-using insects, the egg-shells of terrestrial insects and the silk nests of some terrestrial, ground dwelling spiders.¹²⁻¹⁴

To investigate whether a superhydrophobic material could mimic the plastron action of biological systems we created a sol-gel foam material using methyltriethoxysilane and a phase separation process. Because all pore facing surfaces are methyl terminated, these materials are intrinsically superhydrophobic.¹⁵ When the foam is submerged a silvery sheen can be observed indicating that a film of air remains at the surface of the just as it does at the surface of an insect's plastron. We hollowed out a cylindrical block of foam to create a gas cavity surrounded by porous superhydrophobic walls, analogous to the diving bell of the water spider *Argyroneta aquatica*. The void volume was 2.5 cm³ with walls of approximately 4 mm thick and an external surface area of about 18 cm² (Fig. 1a). We tested our plastron diving bell system by sealing an oxygen sensor inside the gas cavity of the foam and immersing it into an aerated water bath. When the concentration of dissolved oxygen concentration in the water was reduced, the oxygen concentration within the cavity decreased and as the water was re-oxygenated the oxygen level within the cavity increased (Fig. 1b).

In a second experiment, more directly modelling metabolic consumption of oxygen, we placed a zinc-oxygen cell with a resistor across its terminals into the cavity, thereby giving an oxygen consumption rate of 246 $\mu\text{l h}^{-1}$ due to the chemical reaction of

the cell; this is between 7 and 118 times larger than that of a 100 mg spider.¹⁶ The slower decrease and non-zero (~12%) equilibrium value of oxygen levels in the cavity, compared with an equal volume sealed cavity not permitting gas exchange, demonstrates that the foam is working as an external physical gill (Fig. 2). Since arachnids can live in low oxygen levels, a typical 100 mg individual could survive indefinitely within the foam cavity. Moreover, the plastron provided by the foam, scaled down to the surface area of a plastron on the *Argyroneta aquatica* spider, would be sufficient for the spider to indefinitely survive direct submersion in aerated water.

The superhydrophobic plastron we have created demonstrates a general design principle extendable to a wide variety of engineered materials, such as micro or nano-fabricated spikes on a perforated base, which use small-scale topography and hydrophobic chemical functionality to enhance non-wetting into superhydrophobicity.¹⁷ For example, using the data from Journet *et al*¹⁸ for a carbon nanotube forest with 50 nm diameter tubes spaced every 100 nm to 250 nm and a contact angle $\theta = 105^\circ$, we estimate that such a plastron could withstand water penetration to a depth of 37.5 m. The most likely use of our biomimetic plastron would be to supply oxygen for fuel cells to enable miniaturized machines to operate underwater without the need for stored or external supplies of oxygen. It is interesting to note that scaling up the surface area to 90 m², representing a sphere of diameter 2.8 m, suggests enough oxygen could be provided for a human to survive. Moreover, the water-vapor interface of a plastron across which gaseous diffusion occurs, not only allows oxygen to be replenished, but would also prevent a build up of potentially fatal CO₂.

Acknowledgements

The authors acknowledge the help of Ms. Gavalda and financial assistance from the UK EPSRC and MOD/Dstl.

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Figures

Figure 1 Plastron respiration. (a) Schematic of the experiment using the foam with a cavity immersed in water. (b) Response of oxygen level inside a cavity within a superhydrophobic foam (solid curve and left hand y-axis) as the oxygenation of the surrounding water is varied (dashed curve and right hand y-axis).

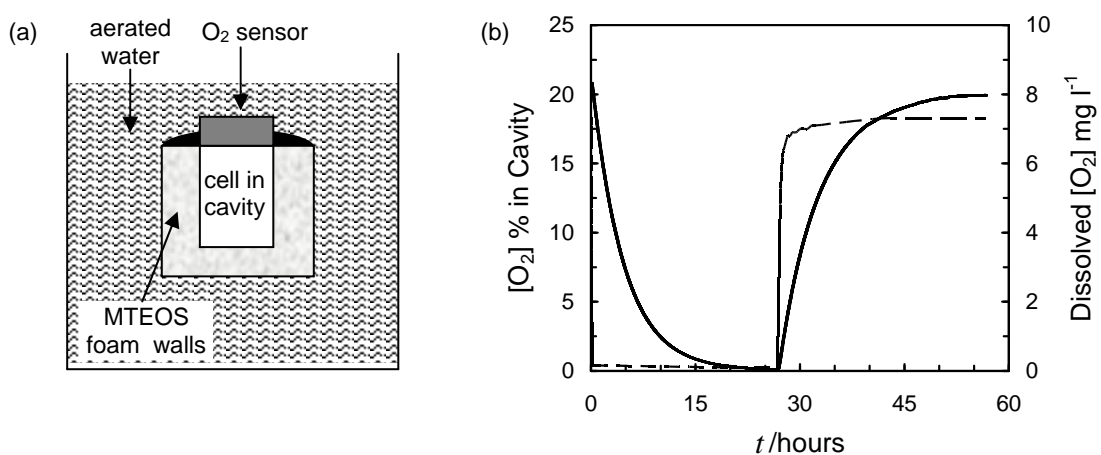
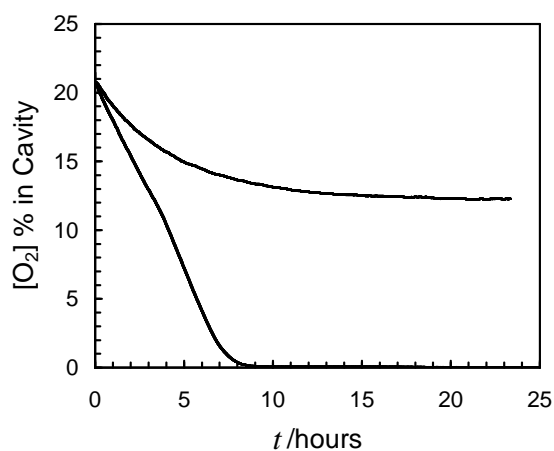


Figure 2 Comparison of oxygen levels between a sealed system (lower curve) and one using the superhydrophobic foam (upper curve) to allow oxygen replenishment during consumption of oxygen at a rate $246 \mu\text{l h}^{-1}$ due to the discharge of a zinc-oxygen cell.



Supplementary Information

Sol-gel preparation: Full details on the preparation and characterisation of the superhydrophobic sol-gel foams are described in reference 1 (see also ref. 2). In brief, 0.1255 moles (25 ml) of methyltriethoxysilane (MTEOS) (98% Lancaster) was added to 0.0018 moles of HCl and 0.83 moles of water or 6.6 equivalents (15 ml of 0.12 M HCl diluted from 37% HCl Analar Aldrich) and 0.327 moles (25 ml) of dimethylformamide (Aldrich) under rapid stirring using a magnetic stirrer. This mixture was sealed and allowed to react for sixty minutes at 22° C. 16 cm³ of ammonia solution, 3.5 M diluted from 35% stock (Fisher), was added to each. The reagents were stirred for a minute before being decanted into 10 ml polypropylene containers and sealed. The materials were left sealed for 20 hours to ensure that they gelled fully before the solvent was exchanged with an excess of methanol (Haymans) 3 changes, 4 days each. The seal was then pricked twice with a scalpel blade (5 mm slits) and the samples allowed to dry at room temperature. This is a reproducible process that creates a material with pore sizes from a few hundred nanometers up to a few micrometers in diameter (depending on solvent and concentration of ammonia used) and a surface with a measured contact angle to water of greater than 150° possessing low contact angle hysteresis. A photograph of the final foam with its cavity is shown in fig. 1s together with an electron micrograph of the pore structure.

Depth Capability: An estimate of depth before a simple capillary tube of radius r is invaded by water can be made from the capillary force around the perimeter supporting the water-air interfacial area: $\Delta p = 2\gamma_{LV}\cos\theta_s/r$ where γ_{LV} is the surface tension of water (72.8 mN m⁻¹) and θ_s is the chemistry determined Young's law contact angle. An order of magnitude estimate using $r \sim 1 \mu\text{m}$ and $\theta_c = 105^\circ$ (typical of hydrocarbons, such as the gels used) gives 37.7 kPa, which implies a depth capability of 3.8 m. For a more general

superhydrophobic surface constructed of hydrophobic posts of cross-sectional area a_h and cross-sectional perimeter p_h arranged in a repeat unit of area A , the water-air interface is distributed across an area $(1-f)A$, where $f=a_h/A$ is the solid fractional area in the Cassie-Baxter model.³⁻⁵ The total force supporting this interface is $p_h\gamma_{LV}\cos\theta_s$. The maximum pressure that the surface can withstand before water intrusion is then,

$$\Delta p = \left(\frac{p_h}{a_h} \right) \left(\frac{f}{1-f} \right) \gamma_{LV} \cos \theta_s \quad (1)$$

For square and circular post shapes, the ratio of perimeter-to-cross-sectional area is $4/d$ where d is the side length and diameter, respectively, and ability to withstand pressure increases rapidly as the post diameter decreases. The depth capability example in the manuscript is inspired by reference 6 and uses equation (1) with vertically aligned 50 nm diameter posts spaced every 100 nm to 250 nm and a contact angle $\theta_s=105^\circ$, to estimate that a plastron could support a pressure up to 368 kPa corresponding to a depth of up to 37.5 m.

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Figure 1s (a) Photograph showing the arrangement of the superhydrophobic foam (with mounted oxygen sensor) used to create a model plastron; for illustration the sectional image shows an internal void with a zinc-oxide cell in another foam block. (b) Scanning electron microscope image of the pore structure of a methyltriethoxysilane foam; the inset shows a magnified view (x 3).

